Syntheses of Antioxidants for Fats and Oils. II : Cresol-analogs of NDGA and Polynuclear Phenolic Antyioxidants

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$$C(ad)+CO_2(ad) \xrightarrow{k_5} 2CO$$

k : velocity constant

(ad): represents the adsorbed state on the reaction vessel surface.

The following equation for the rate of CO formation can be derived from this mechanism with the assumptions that the adsorption of CO_2 exists always in an equilibrium and $k_5 \ll k_3 \ll k_4$,

$$\frac{d[CO]}{dt} = \frac{2\,k_2\,[H_2]}{r_2/k_3+[H_2]}[CO_2],$$

which reproduces our experimental results approximately.

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26. Syntheses of Antioxidants for Fats and Oils. II Cresol-analogs of NDGA and Polynuclear Phenolic Antyioxidants

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The two cresol-analogs of NDGA were prepd. The Grignard reagent of p-bromo-o-cresol methylether was condensed with allyl bromide to p-methoxy-m-methylallylbenzene (I), b_{12} 132–142°. The Grignard reagent of the hydrobromide of (I), b_{13} 132–140°, was treated with I_2, giving meso and racemic mixt. of 1,4-bis (p-methoxy-m-methylphenyl)-2,3-dimethylbutane, b_5 210–215°, meso m. 79–80°. On demethylation with MeMgI and recryst. from benzene, free phenol (II), m. 80–81°, was obtained. p-Cresol allyl ether was rearranged and then methylated to 2-methoxy-5-methylallylbenzene (III), b_{45} 131–132°. Hydrobromide of (III), b_{13} 138–142°, was treated as above, giving 1,4-bis(2-methoxy-5-methylphenyl)-2,3-dimethylbutane, b_{2-3} 195–200°, meso m. 91°, free phenol (IV) m. 163–4°.

The following hindered phenol antioxidants having large molecular size were prepd. The mixt. of 10 g. of 2,6-dimethylol-p-cresol and 39 g. of phenol in 50 ml. of 60% ethanol was saturated with HCl gas at 0°. On standing overnight there resulted white crystals which were filtered and 12 g. of condensate (V), recryst. from acetic acid m. 211–12°, acetate m. 117–18°, was obtained. The determination of the structure is now under way. 2,6-Dimethylol-p-cresol and p-cresol gave crystalline condensate (VI), m. 210–11°, which has probably a four nuclear cyclic structure according to J. B. Niedrel (J. Am. Chem. Soc. **65** 629 (1943)). On similar treatments o-cresol, thymol and eugenol gave amorphous solids (VII), (VIII) and

(IX), with mol. wt. 370–80, 450–65 and 590–600, respectively. Also hydroquinone, hydroquinone monomethyl ether and resorcinol gave resinous products, (X), (XI) and (XII). The mol. wts. could not be determined. 4,6-Dimethylol-o-cresol and p-cresol afforded amorphous solid (XIII), mol. wt. 380–90.

On standing for few days the mixt. of 1 mol of eugenol, equivalent amount of 20% NaOH 2 mol of HCHO as formalin gave yellow viscous oil (XIV), mol. wt. 470–500. Similarly thymol resulted brilliant yellow solid (XV), mol. wt. 550–70.

The activities of these new antioxidants were tested by comparing the oxygen absorption velocities of linseed oil which dissolved the various samples. Crystalline, high melting products, (V) and (VI), were inactive. (IX), (XI) and (XIV) had high activities as Ionol (2,6-di-tert.-butyl-p-cresol). (VII), (VIII) and (XIII) were somewhat weaker than Ionol. Cresol-analogs of NDGA were inactive.

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27. Studies on Chloroalkylethers of Various Alcohols

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I. Some new reactions.

The chlorine atom of choralkylethers of alcohols obtained by the action of formaldehyde and hydrochloric acid upon alcohols, is very reactive, but only a few examples are known till now about the reactions of these compounds.

The authors accordingly tried to elucidate the chemical reactions of these compounds and succeeded in the following reactions.

(1) $C_6H_5OK + ClCH_2OCH_3 \longrightarrow C_6H_5OCH_2OCH_3$ 83% (in ether)

(2) $C_6H_5NH_2 + ClCH_2OCH_3 \longrightarrow C_6H_5NHCH_2OCH_3$ 17% (in ether)

(3) $CH_3COCHCOOC_2H_5 + ClCH_2OCH_3 \rightarrow CH_3COCHCOOC_2H_5$ 30% (in alcohol)
(Na; CH_2OCH_3)

(4) $CH_3OCH_2Cl + ClCH_2OCH_3 \rightarrow CH_3OCH_2CH_2OCH_3$ 50% (Wurz-Fittig's reaction)

(5) $C_6H_6 + ClCH_2OCH_3 \rightarrow C_6H_5CH_2OCH_3$ 23% (Friede-Krafts reaction)

II. Condensation of chloroalkylethers by copper powder into dialkylglycolether

As is well known, the halogenalkyls condense into bi-alkyls by the aid of metalic sodium (Wurz-Fittig's reaction).

This reaction also occurs in the case of chloromethylethylethers of alcohols.

But the authors have discovered that this condensation can be achieved by metalic copper or iron instead of metalic sodium, and the corresponding dialkyl-ethers of glycols were obtained. The results are summerised in the following table.